

## PATENT SPECIFICATION

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NO DRAWINGS.

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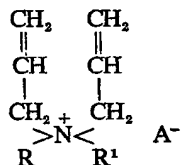
## COMPLETE SPECIFICATION.

## Water-Soluble Copolymers and Process for Preparing Same.

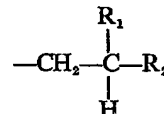
We, CALGON CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of Calgon Centre, Box 1346, Pittsburgh, Pennsylvania 15230, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel highly branched water-soluble copolymers. Specifically, it relates to water-soluble copolymers of (a) diallyl ammonium salts, and (b) other polyunsaturated polymerizable water-soluble monomers.

The diallyl ammonium compounds of this invention have the following general formula:

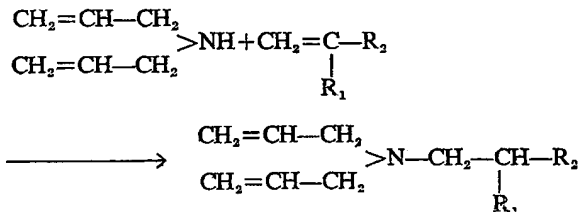


where R is H, alkyl up to 4 carbon atoms or a group of the formula



and where R<sub>1</sub> is H or —CH<sub>3</sub>, R<sub>2</sub> is an electron-withdrawing (activating) group, and R<sub>1</sub> is R or —CH<sub>2</sub>CH<sub>2</sub>OH. Dimethyl diallyl ammonium halide is preferred, but all of the above compounds are included in our invention.

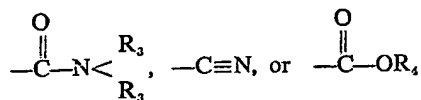
As it is well known in the art, a Michael reaction is the addition of an active hydrogen across an activated double bond. In the case of diallyl amine, the reaction may be expressed



forming a tertiary amine.

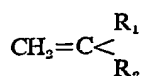
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For purposes of our invention,  $R_2$  may be more specifically defined as



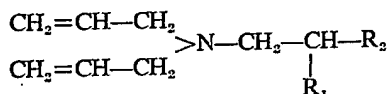
- where each  $R_3$  is independently selected from H, alkyl up to 4 carbon atoms, alkanol up to 4 carbon atoms, or diallyl amino alkyl where each alkyl group contains up to 4 carbon atoms and is independently selected, and  $R_4$  is alkyl up to 4 carbon atoms, alkanol up to 4 carbon atoms, or dialkyl amino alkyl where each alkyl contains up to 4 carbon atoms and is independently selected.  $A^-$  is a noninterfering anion.

- Examples of vinyl type activated double bond compounds of the general formula

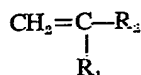


- where  $R_2$  is an electron-withdrawing (activating) group include acrylamide, acrylonitrile, methacrylamide, methacrylonitrile, N,N-dialkylacrylamides, N,N-dialkylmethacrylamides, N-alkanol-acrylamides, N,N-(dialkylamino-alkyl)-methacrylamides, alkyl-acrylates to  $C_4$ , alkyl methacrylates to  $C_4$ , dialkyl amino alkyl acrylates, and dialkyl amino alkyl methacrylates.

The tertiary amine

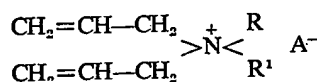


may be prepared by condensation of



- compounds with diallyl amine.

The quaternized version



- may be prepared by reacting the corresponding tertiary amine with a quaternizing agent such as dialkyl sulfate, ethylene oxide, the alkyl halides, sodium chloroacetate, etc.

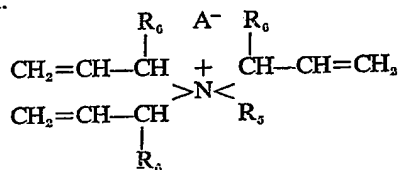
- Polymerization is effected through techniques well-known in the art as examples to follow will illustrate. These diallyl ammonium compounds are believed to undergo cyclization during free radical polymerization to form piperidinium rings. Thus, dimethyl diallyl ammonium chloride would

polymerize to form poly-[N,N-dimethyl-3,5-methylene-piperidinium-chloride].

For detailed examples of the preparation of diallyl ammonium monomers see U.S. Patent Application S.N. 458,753 filed May 25th, 1965.

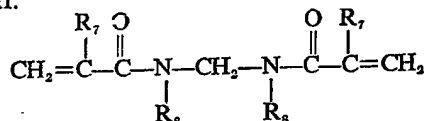
The highly branched water-soluble copolymers of this invention are obtained through the polymerization of a diallyl ammonium salt with any polyunsaturated polymerizable water-soluble compound other than 1,6-diunsaturated allylic systems. We know of no water-soluble compounds having two unsaturated groups, other than the ammonium compounds described above, which will form an uncrosslinked polymer. If any such compound exists, it should be excluded from our second monomer group because it could be expected not to form branches and links between polymer chains. Examples of useful compounds include 1,2-dihydroxyethylenebisacrylamide and compounds of the general formulae:

I.



and

II.



wherein I,  $R_3$  is H, allyl, methallyl, or alkyl having up to 4 carbon atoms,  $R_6$  is H or  $-\text{CH}_3$ , and  $A^-$  is a noninterfering anion, and in II,  $R_7$  is H or  $\text{CH}_3$ ,  $R_8$  is H or alkyl up to 4 carbon atoms. Each  $R_6$ ,  $R_7$ , and  $R_8$  may be independently selected, but it is more usual for each  $R_6$ ,  $R_7$ , and  $R_8$  to be the same. Examples of compounds included in I are triallyl ammonium halide, tetraallyl ammonium halide, methyl triallyl ammonium halide, ethyl triallyl ammonium halide, and tetramethallyl ammonium halide. Examples of compounds included in II include methylenebisacrylamide and methylenebismethacrylamide. Triallyl and tetraallyl ammonium halide and methylenebisacrylamide are preferred.

The polyunsaturated polymerizable water-soluble compound is added to a solution of the diallyl ammonium salt before polymerization. This invention does not contemplate a copolymer of the diallyl ammonium com-

pounds and the polyunsaturated compound to which so much polyunsaturated compound was added before polymerization as to cause the copolymer to pass its gel point.

5 The gel point is the point at which the copolymer has been branched to such an extent by the polyunsaturated compound that it is transformed from a viscous, soluble, fusible liquid to an elastic, insoluble, non-  
10 fusible gel; it is an irreversible reaction. See, for example, "Principles of Polymer Chemistry", by Paul J. Flory, page 47. All of the copolymers contemplated by this invention are water-soluble and therefore have  
15 not been branched beyond their gel point.

The gel point for a given copolymer will depend upon the specific diallyl ammonium compound and the specific polyunsaturated compound used to form the copolymer. If  
20 the diallyl ammonium compound is dimethyl diallyl ammonium halide, the gel point will be reached when about 0.001 mole percent methylenebisacrylamide is used, about 0.055 mole percent triallyl ammonium chloride, or  
25 about 0.001 mole percent tetraallyl ammonium chloride. Other gel points may be determined by experimentation. We prefer copolymers which have been branched as much as possible before reaching their gel  
30 point.

We have performed numerous experiments which demonstrate the production of our copolymers.

#### EXAMPLE I

35 7.5 gms of triallyl amine were neutralized with concentrated HCl to form the hydrochloride salt. This salt was mixed in a reaction vessel with 271 gms of a 52.7% solution of dimethyl diallyl ammonium chloride. The  
40 solution was purged for 1 hr. with nitrogen at 50°—60°C and the temperature was raised to 85°C. A solution of 7.64 gms/100 ml of ammonium persulfate was pumped into the reaction vessel at the rate of 0.5  
45 ml/min. for 100 minutes. The reaction exothermed immediately, the temperature rose to 95°C where it was held for 1 hr. after all the ammonium persulfate was pumped. The final solution concentration was 42.6%. The  
50 resulting copolymer was soluble in water, highly viscous and ideally suitable for coating applications on paper.

#### EXAMPLE II

55 252 gms of a 64% solution of dimethyl diallyl ammonium chloride was placed in a reaction vessel and mixed with 0.05 gm of methylenebisacrylamide. The pH was adjusted to 6.5 and the solution was purged with nitrogen for 1 hr. at 80°C. A solution  
60 of 2.28 gms/100 ml of ammonium persulfate was pumped in at the rate of 0.5 ml/min. for 100 minutes. The reaction exothermed within 9 minutes to 117°C and boiled. The

temperature dropped to 90°C where it was held until all the ammonium persulfate had  
65 been added, and for 1/2 hr. more.

#### EXAMPLE III

The same procedure used in Example II was used here except that 0.07 gm of methylenebisacrylamide was used. The resulting  
70 polymer did not gel but when 0.1 gm of methylenebisacrylamide was used in another experiment, a gel was formed.

#### EXAMPLE IV

A 64% solution containing 252 gms of dimethyl diallyl ammonium chloride was  
75 mixed in a reaction vessel with 0.1 g tetraallyl ammonium chloride. The pH was adjusted to 6.5 and the solution was purged for 1 hr. at 80°C. A solution of 2.28 gm/100  
80 ml of ammonium persulfate was pumped in at the rate of 0.5 ml/min. for 100 minutes. The reaction exothermed to 118°C in 7 minutes, and dropped to 90°C where it was held for 1/2 hr. after all the ammonium per-  
85 sulfate had been pumped in.

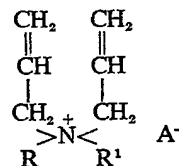
#### EXAMPLE V

The procedure of Example IV was used here except that 0.2 gm tetraallyl ammonium  
90 chloride was used. The copolymer was thicker, but still soluble, indicating the gel point had not yet been reached.

The copolymers of this invention are useful in making electrostatic copy paper for use in electrostatic type copy processes.  
95 Generally, such papers presently contain an upper layer of light-sensitized zinc oxide and a lower layer of an electroconductive material capable of readily dissipating an electrostatic charge. Our novel polymers are readily  
100 applied to paper since they are water-soluble, have improved filming properties, and provide the necessary properties of electroconductivity in the finished paper. Because of  
105 their highly branched structure and the relative absence of low molecular weight segments capable of diffusing into the zinc oxide layer, sharper copies may be made with paper using our copolymers.

#### WHAT WE CLAIM IS:—

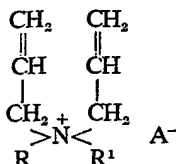
110 1. A water-soluble copolymer of (a) a diallyl ammonium salt of the general formula



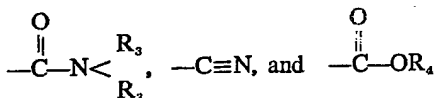
and (b) a water-soluble polyunsaturated  
115 polymerizable compound not containing a 1,6 diunsaturated allylic system. where R is

selected from the group consisting of H, alkyl having up to 4 carbon atoms and a group of the formula  $-\text{CH}_2-\text{CHR}-\text{R}_2$ ,  $\text{R}^1$  is selected from the group consisting of R and  $-\text{CH}_2\text{CH}_2\text{OH}$ , and where  $\text{R}_1$  is selected from the group consisting of H and  $-\text{CH}_3$ ,  $\text{R}_2$  is an electron-withdrawing (activating) group, and  $\text{A}^-$  is a noninterfering anion.

10 2. A water-soluble copolymer of (a) a diallyl ammonium salt of the general formula

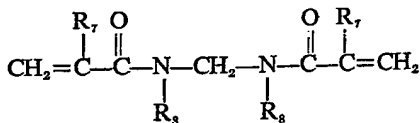


15 and (b) a water-soluble polyunsaturated polymerizable compound not containing a 1,6-diunsaturated allylic system, where R is selected from the group consisting of H, alkyl up to 4 carbon atoms and a group of the formula  $-\text{CH}_2-\text{CHR}-\text{R}_2$ ,  $\text{R}^1$  is selected from the group consisting of R and  $-\text{CH}_2\text{CH}_2\text{OH}$ , and where  $\text{R}_1$  is selected from the group consisting of H and  $-\text{CH}_3$ ,  $\text{R}_2$  is selected from the group consisting of



25 where each  $\text{R}_3$  is independently selected from the group consisting of H, alkyl having up to 4 carbon atoms, alkanol having up to 4 carbon atoms, and dialkyl amino alkyl where each alkyl contains up to 4 carbon atoms and is independently selected,  $\text{R}_4$  is selected from the group consisting of alkyl up to 4 carbon atoms, alkanol up to 4 carbon atoms, and dialkyl amino alkyl where each alkyl contains up to 4 carbon atoms and is independently selected, and  $\text{A}^-$  is a noninterfering anion.

3. The copolymer of claim 1 or 2, wherein said water-soluble polyunsaturated polymerizable compound is a compound of the general formula

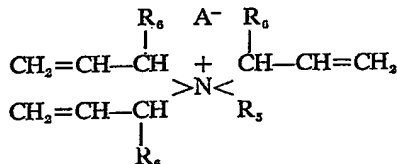


where each  $\text{R}_7$  is independently selected from the group consisting of  $-\text{H}$  and  $-\text{CH}_3$  and each  $\text{R}_8$  is independently selected from H and alkyl up to 4 carbon atoms.

4. The copolymer of claim 1 or 2, wherein said water-soluble polyunsaturated poly-

merizable compound is methylene bisacrylamide.

5. The copolymer of claim 1 or 2, wherein said water-soluble polyunsaturated polymerizable compound is a compound of the general formula

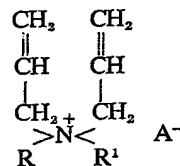


where  $\text{R}_5$  is selected from the group consisting of H, allyl, methallyl, and alkyl up to 4 carbon atoms, each  $\text{R}_6$  is independently selected from the group consisting of H and  $-\text{CH}_3$ , and  $\text{A}^-$  is a noninterfering anion.

6. The copolymer of claim 1 or 2, wherein said water-soluble polyunsaturated polymerizable compound is triallyl ammonium halide.

7. The copolymer of claim 1 or 2, wherein said water-soluble polyunsaturated polymerizable compound is tetraallyl ammonium halide.

8. A process for producing water-soluble copolymers which comprises reacting (a) a diallyl ammonium salt of the general formula



where R is selected from the group consisting of H, alkyl having up to 4 carbon atoms and a group of the formula  $-\text{CH}_2-\text{CHR}-\text{R}_2$ ,  $\text{R}^1$  is selected from the group consisting of R and  $-\text{CH}_2\text{CH}_2\text{OH}$ , and where  $\text{R}_1$  is selected from the group consisting of H and  $-\text{CH}_3$ ,  $\text{R}_2$  is an electron-withdrawing (activating) group, and  $\text{A}^-$  is a noninterfering anion, with (b) a water-soluble polyunsaturated polymerizable compound not containing a 1,6-diunsaturated allylic system under polymerizing conditions.

9. The process for producing water-soluble copolymers substantially as described in any one of the examples.

10. Water-soluble copolymers whenever prepared by the process described herein or by any process consisting of an obvious chemical equivalent thereof.

For the Applicants,  
F. J. CLEVELAND & COMPANY,  
Chartered Patent Agents,  
Lincoln's Inn Chambers,  
40-43 Chancery Lane,  
London, W.C.2.